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# Role of Mixing and Rheology in Reactive Extrusion

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To understand the performance of multicomponent reactions in extruders, the mixing mechanism in the extruder has to be understood. Viscosity and quantity differences between the components fed to the extruder considerably influence this mixing process. The extent of their influence on the mixing and therewith the reaction process was investigated with a decolorization reaction in a fully intermeshing counterrotating twin screw extruder with a transparent barrel. It could be concluded that for this type of extruder faster mixing is achieved if one component (mostly a side feed) consists of low viscous material and is present in considerable amounts. Thus an increase in the viscosity ratio between both components leads to a decrease of the mixing length and an increase of the quantity ratio leads to an increase of the mixing length. The experimental results agreed well with the theoretical analysis of the flow behavior in the mixing areas of the extruder.

## Introduction

Over the past years interest in the use of an extruder as a polymerization reactor has increased considerably within industry. The main advantage of the use of twin screw extruders, compared to conventional reactors, is the possibility of solvent-free polymerization, making extra separation steps superfluous. Due to the absence of solvent the process also becomes more energy efficient and environment friendly. Some other advantages are their relative insensitivity to viscosity changes, a large heat exchanging surface, and well-defined shear levels. The polymerization reactions which have been performed to date in an extruder are presented in Table 1 (Wielgolinski and Nangeroni, 1983; Brown and Orlando, 1988; Ganzeveld and Janssen, 1992, 1993).

From a process technology point of view, all these reactions can be divided into two main groups; namely the single-component and the multicomponent reactions.

1. The single-component reactions occur throughout the bulk of the material as only one component or an ideal mixture of two or more components is present. For this group of reactions, macromixing over the length of the extruder and the temperature of the reacting mixture play an important role. Both parameters determine the progress of the reaction in the extruder. An example of this type of reaction is the polymerization of butyl methacrylate (Ganzeveld and Janssen, 1993).

2. The multicomponent reactions, on the other hand, are strongly influenced by micromixing as the reaction proceeds at the interface between the components. Normally, this type of reaction becomes diffusion limited as the reaction progresses due to the buildup of reaction product. To overcome the diffusion limitation, extensive micromixing is necessary. In addition to micromixing, these reactions are also influenced by the aforementioned macromixing and the temperature of the reaction mixture. Examples of this type of reaction are the polymerization of urethanes and the grafting of maleic anhydride on high-density polyethylene (Ganzeveld and Janssen, 1992, 1992a).

Therefore, to model the extruder as a polymerization reactor for multicomponent reactions, the mechanism of mixing has to be studied and understood. In particular the mixing of liquids with different viscosities in different quantity ratios has to be examined as in polymer processes combinations of these situations often occur.

Table 1. Reactions Performed in the Extruder

type of reaction	end products
bulk polymerization	polyether imide
condensation	polyesters PET (poly(ethyl terephthalate)) PBT (poly(butyl terephthalate)) polyamide 6.6 polyarylate
addition	polyurethanes polyamide 6 polyoxymethylene PMMA (poly(methyl methacrylate)), PBMA acrylic copolymers styrene copolymers water-soluble polyamide
graft reactions and functionalization reactions	graft copolymer of polystyrene and maleic anhydride graft copolymer of polyolefins and vinylsilanes graft copolymers of polyolefins and acrylic and methacrylic monomers graft copolymer of EVA <sup>a</sup> with acrylic acid graft copolymer of polyolefins and maleic anhydride halogenation of polyolefins or EVA especially chlorination
interchain copolymer formation	copolymer of reactive polystyrene and polymers with amine, mercaptan, epoxy, hydroxy, anhydride, or often carboxylic acid groups copolymer of polypropylene grafted with maleic anhydride and nylon-6 copolymer of polystyrene and polyolefins copolymer of EVA grafted with methacrylates and grafted polystyrene
coupling reactions	coupling of PBT with diisocyanate and polyepoxide or polycarbodiimide coupling of PET with bis(2-oxazoline)
degradation reactions	degradation of polypropylene by shear-heating degradation of PET with ethylene glycol

<sup>a</sup> Ethylene-vinyl acetate copolymer.

## The Counterrotating Twin Screw Extruder

The counterrotating twin screw extruder studied in this article is closely intermeshing and therefore consists of series of C-shaped chambers (Figure 1) in which material is transported toward the die (Janssen, 1978). The volumetric displacement rate or theoretical throughput of the extruder equals the number of C-shaped chambers

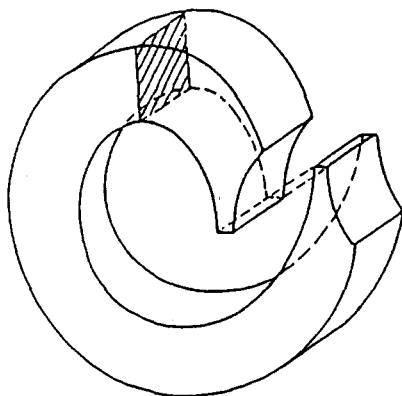


Figure 1. The C-shaped chamber.

transported per unit time multiplied by the chamber volume:

$$Q_{th} = 2mNV \quad (1)$$

in which  $N$  is the screw speed,  $m$  the number of thread starts per screw, and  $V$  the volume of a C-shaped chamber.

The real throughput of the extruder is determined by the amount of material fed to the screws. In the fully filled zone this real throughput is usually smaller than the volumetric displacement rate of the screws. The difference corresponds to a backward leakage flow in the extruder through the leakage gaps. Therefore, the real volumetric throughput is given by

$$Q = Q_{th} - Q_1 \quad (2)$$

where  $Q_1$  is the sum of all leakage flows over a cross section of the extruder.

The leakage flow can be written as the summation of a drag component and a pressure component:

$$Q_1 = AN + B \frac{\Delta P_i}{\eta_i} \quad (3)$$

where  $A$  and  $B$  are geometrical constants,  $\Delta P$  is the pressure difference between two chambers,  $\eta$  is the viscosity of the material, and the index  $i$  concerns the  $i$ th chamber.

The leakage flows through mechanical clearances between the two screws and between the screws and the barrel: the leakage gaps. These gaps connect consecutive chambers on the screws resulting in an interaction of flow and material in the various chambers (Figure 2). The leakage flows can strongly affect the flow profile and therefore the mixing and residence time distribution of material in each individual chamber (Speur et al., 1987). The leakage gaps can be divided into four groups (Janssen, 1978):

1. The flight gap ( $Q_f$ ). This is a clearance between the barrel and the flight of the screws.
2. The tetrahedron gap ( $Q_t$ ). Between the flight walls a gap exists having approximately the shape of a tetrahedron. This gap connects the consecutive chambers on the opposite screws.
3. The calender gap ( $Q_c$ ). This gap is formed by the clearance between the flight of one screw and the bottom of the channel of the other screw and resembles a calender.
4. The side gap ( $Q_s$ ). This is a gap between the flanks of the flights of the two screws perpendicular to the plane of the screw axes.

### The Mixing Mechanism in the Counterrotating Extruder

Mixing in a counterrotating twin screw extruder occurs in two distinct regions of the extruder, namely, in the

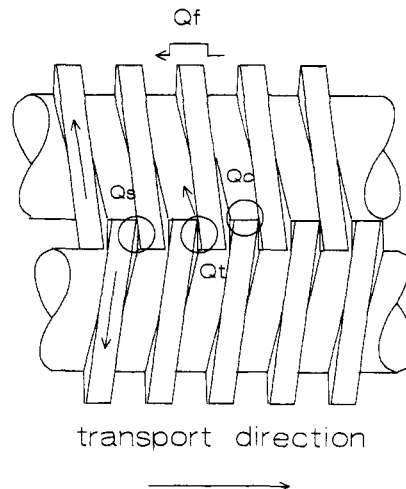


Figure 2. Leakage gaps in a counterrotating closely intermeshing twin screw extruder.

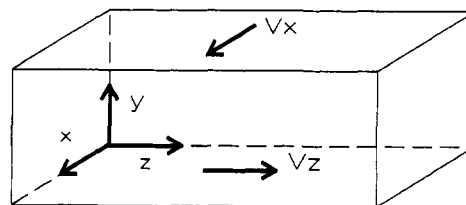


Figure 3. Rectangular representation of the chamber.

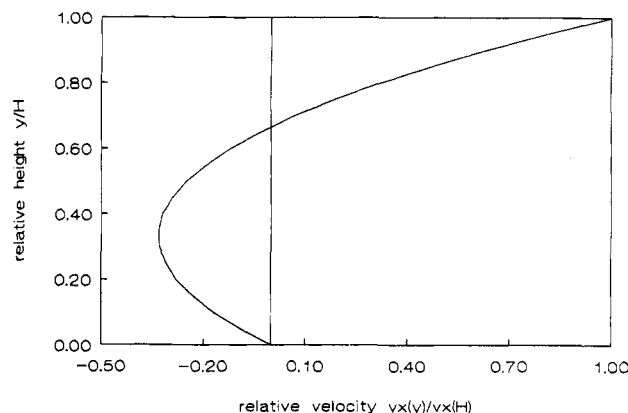
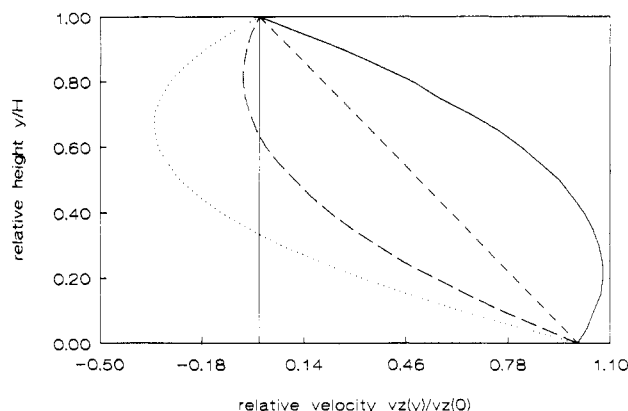


Figure 4. Velocity profile in the cross chamber direction.

chambers and in the leakage gaps. In the chambers, macromixing and redistribution of material occurs. In the leakage gaps, high shear levels are present, leading to a decrease in striation thickness, thereby enhancing micromixing.

**The Mechanism in the Chamber.** The mixing mechanism in the chamber is dependent upon the helical flow of a fluid element in the chamber. The helical flow is caused by the movement of the chamber as a result of the rotation of the screw and the pressure drop over the chamber. The helical flow can be subdivided into two velocity components: a velocity in the  $x$ -direction (the cross chamber velocity) and a velocity in the  $z$ -direction (the down chamber velocity). To be able to analyze the flow within the chamber, the C-shaped chamber has been modeled as a rectangle (Figure 3) (Speur, 1988).

The cross chamber velocity consists of a circulating flow with, in case of a negligible flight leakage, a zero net throughput. Due to this flow pattern a stagnation point exists at two-thirds the height of the chamber around which the material circulates (Figure 4). The down chamber velocity profile is dependent on the amount of leakage



**Figure 5.** Velocity profiles in the down chamber direction. (---,  $\alpha_1 = 0$ ; --,  $\alpha_1 = 0.3$ ; - · -,  $\alpha_1 = 0.63$ ; —,  $\alpha_1 = 1.0$ .)

flow. A large leakage flow results in all material flowing toward the gaps. If, on the other hand, the leakage flow is small, almost no material is able to leave the chamber. Therefore, the material will circulate longitudinally in the chamber. In this case, the down chamber profile shows a circulating flow similar to the cross chamber profile (Figure 5). The combination of the down chamber profile and the cross chamber profile leads to the helical flow which causes the macromixing and redistribution.

**The Mechanism in the Gaps.** In the leakage gaps, shear flows and elongational flows are present. Both lead to a decrease in the striation thickness thereby enhancing the micromixing. As multicomponent reactions take place at the interface between the components, the enhanced micromixing results in an enhanced reaction and therefore in a decrease of the necessary reaction length in the extruder.

### Mixing Parameters in the Extruder

On the basis of the mechanism of mixing in this type of extruder, it can be concluded that micromixing mainly occurs in the gaps. Experimentally, this was verified, the passage of material through high shear and elongational flow fields is necessary to increase the micromixing and to perform the multicomponent reactions (Speur and Janssen, 1984).

The number of passages needed for the completion of the reaction is determined by the striation thickness achieved and the diffusion coefficient of the reactive components. Both factors are influenced by the magnitude of the shear forces, the viscosity and quantity ratio of the components, and the rearrangements of the material after a gap passage as we will show later.

**The Mixing Efficiency and the Mixing Deficiency.** From the principle of distributive mixing stated above, two relevant mixing parameters were developed that were also applicable to other types of extruders (Ganzeveld and Janssen, 1992): (1) the mixing efficiency, being the average number of passages of a fluid element through a high shear region and therefore the number of times the material undergoes extensive micromixing; (2) the mixing deficiency, defined as the fraction of material that does not pass through these high shear regions and, consequently, does not undergo extensive micromixing.

With this definition of the mixing parameters, the amount of micromixing arising from the low shear regions is neglected as it is very small compared to the extent of micromixing occurring in the high shear regions.

In a counterrotating closely-intermeshing twin screw extruder, the regions with high shear and elongational

flows are found in the leakage gaps of the extruder as stated before. For multicomponent reactions which start with low viscous materials, all the leakage gap passages are efficient to increase the micromixing of the materials. However, for multicomponent reactions that start with viscoelastic materials, such as grafting reactions, the area in which the shear and elongational flows are effective for the reaction is largely limited to the reaction zone.

Therefore, the mixing efficiency for multicomponent reactions with viscoelastic materials equals the number of gap passages of a particle in the reaction zone. For multicomponent reactions which start with low viscous reactive materials, the mixing efficiency is equal to the number of gap passages in the total extruder. The mixing deficiency equals the amount of material that does not leave the C-shaped chamber in the reaction zone or the total extruder. Therefore, the leakage flows completely determine the mixing efficiency and deficiency.

This leads to the following equations for the mixing efficiency and the mixing deficiency for a counterrotating extruder (Ganzeveld and Janssen, 1992); the mixing efficiency equals

$$E = \frac{BQ_1}{2K(Q_1 - AN)} + \frac{\nu_r AN}{2Q} - \frac{BAN}{2K(Q_1 - AN)} \quad (4)$$

with  $K$  the reciprocal die resistance and  $\nu_r$  the number of chambers in the reaction zone.

This equation can be simplified to

$$E = \frac{B}{2K} + \frac{\nu_r AN}{2Q} \quad (5)$$

Thus, the mixing efficiency of the total extruder depends on the geometrical constants  $A$  and  $B$ , the reciprocal die resistance  $K$ , the number of chambers in the reaction zone  $\nu_r$ , the throughput  $Q$ , and the rotation rate of the screws  $N$ .

The mixing deficiency for the extruder is equal to

$$D = \exp\left\{-\alpha_r \left(\frac{B}{2K} + \frac{\nu_r AN}{2Q}\right)\right\} = \exp\{-\alpha_r E\} \quad (6)$$

As the mixing deficiency is related to the mixing efficiency, it also depends on the same parameters and the relative throughput  $\alpha_r$ .

The developed mixing model is useful to approximate the amount of mixing in the extruder. However, it implicitly assumes a constant viscosity of the mixture and equal viscosities and quantities of the components. This situation rarely occurs in real polymerization reactions where the mixing of liquids with different viscosities in different amounts is often needed.

### Mixing with Different Viscosities

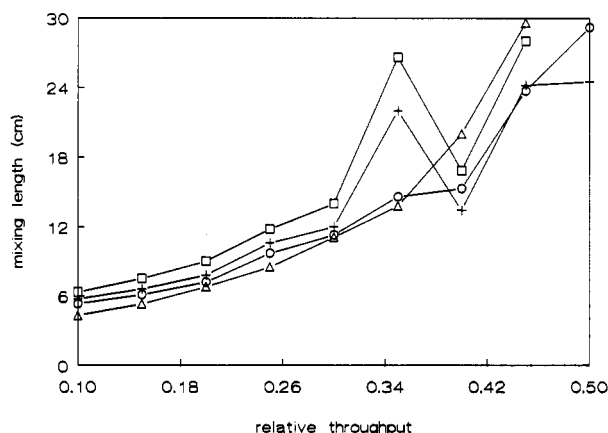
The influence of viscosity and quantity differences between components on the flow behavior and therewith the mixing behavior was investigated. The change of the flow behavior in the chamber and the gaps due to the viscosity and quantity differences was first experimentally determined and then analyzed theoretically.

### Experiments

To check the influence of viscosity and quantity differences on the necessary reaction length (mixing length) in the extruder, an acid-base decolorization with an indicator, thymol blue, was performed in a counter-

**Table 2. Geometrical Dimensions of the Experimental Extruder**

$R$	screw radius	0.035 m
$S$	pitch	0.02 m
$H$	chamber height	0.01 m
$B_f$	flight width	0.0075 m
$\sigma$	calender gap width	0.0025 m
$\psi$	flight wall angle	14°
$V_c$	chamber volume	17.59 cm <sup>3</sup>

**Figure 6.** Influence of viscosity ratio of components on mixing length (quantity ratio 1:1). (Viscosity ratio:  $\square$  = 1:1,  $+$  = 1:2,  $\circ$  = 1:5,  $\Delta$  = 1:10.)

rotating twin screw extruder equipped with a transparent barrel. The geometrical data of the extruder are given in Table 2.

The viscous fluid used was glycerin mixed with different amounts of water. Viscosity ratios of 1:1, 1:2, 1:5, and 1:10 were used. Likewise, the quantity ratios of the components were changed from 1:1, 1:2, 1:5, and finally to 1:10.

The total amount of acid present in the minor component has been kept constant to assure a constant reaction rate. In all experiments the minor component was the low viscous fluid.

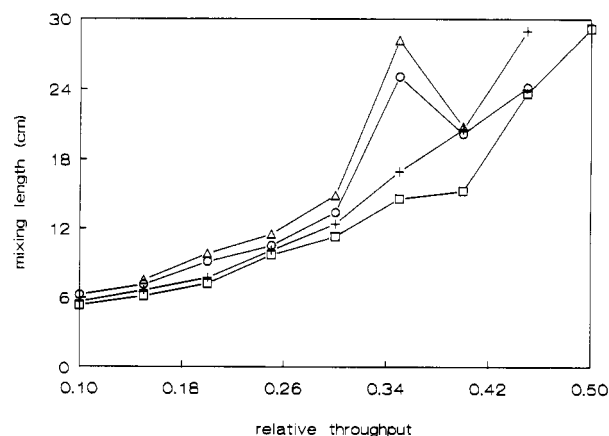
The mixing length, and therefore the mixing time, needed for the reaction to be completed was determined as a function of the relative throughput  $\alpha_r = Q/Q_{th}$ . This relative throughput was varied by changing the feed rate of the extruder ( $2.5 \times 10^{-3}$  to  $10 \times 10^{-3}$  m<sup>3</sup>/h) while the screw speed was kept constant at 0.2 s<sup>-1</sup>.

The mixing or reaction length has been defined as the length from the beginning of the extruder up to the point where no blue color could be detected.

## Results

Examining the results, as the viscosity of the minor component is changed (Figure 6), it becomes clear that the mixing length decreases if the viscosity of the minor component decreases. A lower viscous side feed obviously will have a positive effect on the mixing and therewith the reaction process. This implicates that the mixing process in the extruder changes due to the presence of two components with different viscosities. This change in mixing (flow behavior) can either occur in the chamber, where the macromixing may be affected, or in the gaps, where different flow patterns can occur for either of the components. The change of flow behavior in the extruder will be analyzed in the next paragraph to explain the experimental results.

The experiments concerning the changes in the quantity ratio result in an increase of the mixing length as the amount of low viscous material present decreases (Figure 7), probably again due to a change in the mixing process.

**Figure 7.** Influence of quantity ratio of components on mixing length (viscosity ratio 1:5). (Quantity ratio:  $\square$  = 1:1,  $+$  = 1:2,  $\circ$  = 1:5,  $\Delta$  = 1:10.)

From the experiments also a peak in the mixing length becomes visible present, in all the graphs, at a relative throughput of 0.35. Obviously, the mixing (reaction) process is disturbed. Unreacted material must be partially blocked in going through the gap, leading to the visible increase in the time needed for mixing.

The only explanation possible is that reacted material entering the chamber through a gap is, again, exactly in front of the calender gap as it has gone through the chamber, thereby obstructing unreacted material to pass through the gap.

To verify the assumption, the flow of the reacted material in the chamber was calculated. It appeared that the reacted material entering the chamber at the height of the calender gap was in front of the other calender gap after completing one helix in the chamber. In the case of the extruder used, this is only true for a relative throughput of 0.35. As a consequence, the peak does not appear at other throughputs.

## Theoretical Analysis of the Experimental Results

To explain the experimental results, the flow situations in the chamber and in the gap when two components with different viscosities and in different quantities are present were analyzed and calculated.

**Mixing Mechanism in the Chamber.** First the flow behavior in the chamber was examined. The calculations were based on the assumption that the liquid with the lowest viscosity is situated near the walls initially. This agrees both with a common practice that a low viscous minor component is fed through a side stream as well as with the general contention that low molecular material has a tendency to accumulate in regions of high shear. Therefore, the high viscous liquid is supposed to be surrounded by the low viscous liquid (Figure 8).

The mixing mechanism in the chamber is known to be dependent on the helical flow of the material causing macromixing and redistribution. What happens with this helical flow if two liquids with different viscosities are present in the chamber?

The normal situation for the flow, if two liquids with equal viscosities are present in the chamber, is described in the mixing mechanism. The cross chamber velocity shows a circulating flow around the stagnation point at two-thirds the height of the chamber. The down chamber velocity profile is dependent on the amount of leakage flow.

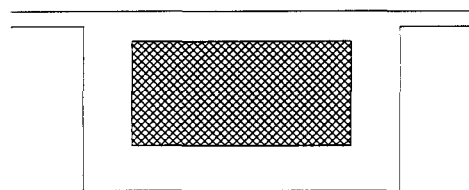


Figure 8. Two liquids with a different viscosity in the chamber.

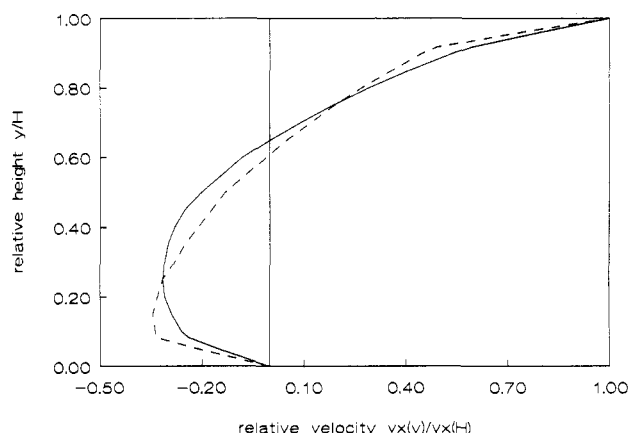


Figure 9. Change of the cross chamber velocity profile for different viscosity ratios (quantity ratio 1:5). (Viscosity ratio: — = 1:2, --- = 1:5.)

With liquids with different viscosities present in the chamber, it is calculated that the down chamber velocity profile does not change significantly. The down chamber velocity profile can thus be assumed to remain the same. However, in the cross chamber direction, the profile changes considerably depending on the viscosity ratio of the liquids (Figure 9).

The stagnation point or zero velocity point which, in the normal situation, is present at two-thirds the height of the chambers drops to a lower height. As the down chamber profile has not changed significantly, this implies that for the new stagnation point the average down chamber velocity is larger than it was at two-thirds of the height (see Figure 4). If the assumption now still holds that the particle staying at the height of the zero velocity point in the cross chamber direction is the last particle to leave the chamber (Speur and Janssen, 1984), it can be concluded that the residence time of the slowest particle in the chamber decreases. This inevitably leads to a decrease in the mixing length.

Thus, decreasing the viscosity of the minor component leads, for the flow in the chamber, to a drop of the zero velocity point, an increase of the lowest down chamber velocity, a decrease in the residence time of the slowest particle in the chamber, and a decrease in the mixing length.

The decrease of the amount of the minor component resulted in a change of the velocity profile in the chamber, but no significant drop of the zero velocity point could be detected.

**Mixing Mechanism in the Gaps.** To investigate the influence of liquids with different viscosities on the flow in the calendar gap, we restrict ourselves to the region close to the nip. Under the normal assumptions of the

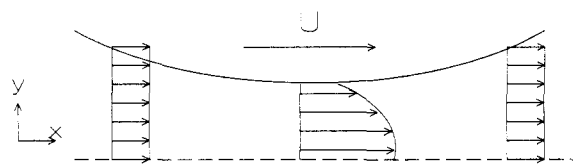


Figure 10. Flow profile in the calendar gap.

Table 3. Shear Rate of the Low Viscous Component Compared to the Shear Rate of the High Viscous Component in the Calendar Gap

viscosity ratio	quantity ratio of minor component to major component			
	1:1	1:2	1:5	1:10
1:1	3.0:1	2.5:1	2.2:1	2.1:1
1:2	6.0:1	5.0:1	4.4:1	4.3:1
1:5	15.0:1	12.5:1	11.0:1	10.5:1
1:10	30.0:1	24.9:1	22.0:1	21.0:1

lubrication approximation, we can approximate the flow through the calendar gap in this area by the classical calendar theories (Gaskell, 1950). Between the rollers, three layers of material are present: one high viscous layer surrounded by two low viscous layers. Normally, the flow in the calendar gap is represented by Figure 10 and the formula for the velocity equals

$$V_z = U + \frac{1}{2\eta} \frac{dP}{dz} (y^2 - H^2) \quad (7)$$

where  $U$  is the average velocity of the screw surfaces involved,  $\eta$  the viscosity,  $dP/dz$  the pressure gradient in the calendar gap, and  $H$  the height of the calendar gap.

By calculating the average shear rate of each layer, the influence of viscosity and quantity differences can be examined. The results are presented in Table 3. From the results in the table, the following can be concluded:

1. The decrease of the viscosity of the minor component leads to an increase in the velocity ratio of the minor component to the major component.
2. A decrease in the amount of low viscous material present results in a decrease of the velocity ratio.

The consequences of conclusion 1 are a decrease of the viscosity of the minor component leads to a better mixing and a shorter mixing length due to a larger contact area and a decrease in the striation thickness.

The consequences of conclusion 2 are a decrease of the amount of minor component leads to an increasing mixing length due to a relative increase in the striation thickness.

Combining the conclusions of the theoretical modeling leads to the following: a decrease in the viscosity of the minor component leads to a decrease in the mixing length; a decrease in the amount of low viscous material present leads to an increase of the mixing length.

We see that the experimental results can qualitatively be explained well by an analysis of the changes in flow behavior in the mixing areas in the extruder.

## Conclusions

Micromixing plays an important role in performing multicomponent reactions in extruders. The amount of micromixing in an extruder can be related by two parameters: the mixing efficiency and the mixing deficiency. These two parameters give a first approximation of the amount of micromixing present in the extruder and therefore can be used in designing the length of the reaction zone. This simple model does not yet account for viscosity and quantity differences between the components.

Experiments prove that these, often existing, differences can influence the mixing process in the extruder considerably. Therefore, these factors have to be taken into account in the future modeling of the mixing and the multicomponent reactions. The consequences in reactive extrusion, with a fully intermeshing counterrotating twin screw extruder, for mixing a side feed (being a monomer, catalyst or initiator stream) are the following:

1. Faster mixing is achieved if the side feed consists of low viscous material.
2. Mixing is improved if the amount of side feed is increased.
3. Certain combinations of screw design and operating conditions may result in an unexpected strong decrease of the mixing efficiency.

However, these conclusions apply only to the completely miscible system researched. In not completely miscible systems, where interfacial tensions exist, different results may occur.

### Acknowledgment

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### Nomenclature

$A$  = geometrical constant,  $m^3$   
 $B$  = geometrical constant,  $m^3$   
 $D$  = mixing deficiency  
 $E$  = mixing efficiency  
 $H$  = height of the chamber,  $m$   
 $K$  = reciprocal die resistance,  $m^3$   
 $L_r$  = reaction length,  $m$   
 $m$  = number of thread starts  
 $N$  = screw speed,  $s^{-1}$   
 $\Delta P$  = pressure difference between C-shaped chambers,  $Pa$   
 $\Delta P_i$  = pressure difference between chambers at position  $i$ ,  $Pa$   
 $Q$  = throughput,  $m^3/s$   
 $Q_1$  = theoretical throughput,  $m^3/s$

$Q_{th}$  = theoretical throughput,  $m^3/s$   
 $U$  = rotation velocity of the screws,  $m/s$   
 $V$  = chamber volume,  $m^3$   
 $V_z$  = flow velocity in the calender gap,  $m/s$   
 $\alpha_l$  = relative leakage flow  
 $\alpha_r$  = relative throughput  
 $\eta$  = viscosity of the material,  $Pa \cdot s$   
 $\eta_i$  = viscosity of the material at position,  $Pa \cdot s$   
 $\nu_r$  = total number of chambers in the reaction zone

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